

## ANTI-RUST COATING

### FIELD OF THE INVENTION

This invention relates to rust converting and rust inhibiting coatings.

### BACKGROUND OF THE INVENTION

Many compositions for removal and inhibition of corrosion are known in the literature. Some examples of such compositions are listed below.

US 4,462,829 describes a rust converting and rust inhibiting primer, which comprises an aqueous suspension or aqueous emulsion of alkyd resin, pigments, a drying accelerator and a surfactant, and may be thinned by non-polar solvents such as petroleum spirits.

US 5,312,491 describes rust inhibiting compositions that contain oxime compounds as a rust converter and have improved elasticity.

US 5,476,890 describes a water thinnable primer, effectively adherent to rusted metal substrates that has a neutral pH of around 7.

US 4,086,182 describes a rust transforming composition comprising an aqueous dispersion of a synthetic binding agent, a polymeric esterification product and acid anhydrides. Upon application to rusty iron the composition gives deep black lacquer-like corrosion-resistant film.

EP 0 264 471 describes a coating composition applicable to hot metal surfaces between 40 and 250°C, without prior chemical conversion.

## SUMMARY OF THE INVENTION

The invention provides, according to one of its aspects, an acidic water thinnable composition for rust conversion and corrosion inhibition. The composition may be used as a paint or a primer. The application of the composition  
5 of the invention to a rusted surface results in rust conversion and generation of an elastic passivation film, which exhibits strong adhesion to the metal surface.

In this context acidic means having a pH of less than 5, preferably between 2.5 and 3.5. The acidity of the composition of the invention is advantageous since it allows a most efficient rust converting. Thus, the composition of the invention may  
10 be used for treating rust layers of more than 20 $\mu$ m thickness, and some compositions according to the invention are suitable for treating rust layers of more than 50 $\mu$ m. As the treated rust layer is thicker a larger number of composition layers may be required.

The composition according to the invention typically shows very high  
15 thermal stability, and deformations are found to occur only around 250°C to 400°C, depending on the specific embodiment. The minimum film forming temperature (MFFT) of compositions according to the invention is typically 5°C and in some embodiments may be as low as 0°C.

Consequently, the composition according to the present invention is  
20 applicable at temperatures of 30°C and below, such as room temperature, 5°C and 0°C.

The composition of the invention creates a coating, which is capable of simultaneously acting as bonding, inhibiting and protecting layer. The coating includes the products of the reaction between the coated object (whether rusted or  
25 not) and the composition. The coating thus formed is strong and self-curing, and under normal environmental conditions requires no additional protective lacquer/paint overcoat and may be used as an uppermost paint layer. Furthermore, the coating may be used as a primer, since it may be easily over-coated with a wide variety of paints in order to manipulate its final color, or in order to provide it with  
30 additional protection. Such additional protection may be needed when the coating is

used under severely corrosive environmental conditions, for example, when the coated objects are ducts for corrosive chemicals.

According to a further aspect of the invention, the composition of the present invention is used as a primer. The primer is applicable over rusted objects  
5 having various degrees of rust ranging up to at least 100 microns, without pre-treating for removing the rust. Cleaning the object from dust and oil before the coating may be carried out by washing with water, seawater, or water containing detergents.

The primer according to the invention may be applied on objects made of  
10 steel, iron, cast iron, galvanized iron, aluminum, and the like. The composition of the invention either used as a paint or as a primer, comprises alkyd resins, an acid, iron oxide pigment, and a stabilizer. Typically, the composition according to the invention also comprises additives, fillers, surfactants, thickeners and additional pigments.

15 The alkyd resin is preferably a water emulsion of acrylic resins, vinyl resins, polymers and mixtures thereof. Its solid content is preferably from 45% to 55%.

The acid is preferably phosphoric acid.

The iron oxide,  $\text{Fe}_2\text{O}_3$ , is at least 2% (w/w) of the composition of the invention, preferably 7%.

20 Non-limiting examples of stabilizers that may be useful in preparing a composition according to the invention are propanol, propylene glycol, anhydride ions of phosphor and fluorine, and mixtures thereof. Several commercially available stabilizers that were found to be suitable for use according to the present invention are DISPEX™, manufactured by CIBA Speciality Chemicals of Basel,  
25 Switzerland, BYK 154, produced by BYK Chemie GmbH, Wesel, Germany; and WRACLA™, manufactured by the PCI GROUP, USA. As shown below, WRACLA™ is most preferable.

Suitable fillers should be acidic (of pH 5 and below) and may include, but are not restricted to silicon oxide and barium sulfate.

As well known in the art, surfactant compositions may be added to the composition in order to prevent it from creating bubbles, to enhance its flexibility, and the like. Non-limiting examples to these are the commercially available BYK-036, BYK-190, and BYK-380, all manufactured by BYK-Chemie GmbH of  
5 Wesel, Germany.

A non-limiting example of a thickener suitable for use in accordance with the present invention is hydroxyethylcellulose.

Additives that may improve the quality of the composition of the present invention are inorganic salts, typically chlorides, phosphates and sulfates of alkali  
10 and earth alkaline metals, preferably NaCl, MgCl<sub>2</sub>, and MgSO<sub>4</sub>. Such additives improve the composition stability under severe humidity conditions. One way to provide such additives to the composition is to replace at least part of the water with seawater.

According to another aspect of the present invention there is provided an  
15 object that is coated with a composition according to the invention. Objects that may be coated by the composition of the invention include, but are not restricted to objects made of iron, cast iron, aluminum, steel, galvanized steel or galvanized iron.

According to another aspect of the present invention there is provided a  
20 method for protecting an object from corrosion and converting rusty portions thereof into non-corrosive portions, the method comprising coating the object with the composition of the invention.

According to yet another aspect of the present invention there is provided a method for treating a rusty object before painting, the method comprising washing  
25 the object with a suitable cleaning solution and coating the washed object with at least one layer of a composition according to the invention. Preferably, the cleaning solution is selected from water, seawater and detergent containing water.

## BRIEF DESCRIPTION OF THE FIGURES

Fig. 1A and its continuation, Fig. 1B, show a table of the test results of 11 panels coated with a composition according to the invention and commercially available primers and paints.

5 Fig. 2A is a photograph of a rusty panel painted with Amerlock 400 epoxy paint.

Fig. 2B is a photograph of a rust-clean panel painted with Tambour® antirust primer and Amerlock 400 epoxy paint.

10 Fig. 2C is a photograph of a rusty panel painted with two layers of the primer of the invention and Amerlock 400 epoxy paint.

Fig. 3A is a photograph of a sandblasted panel painted with Nirlat Zinchromate primer and Nirlat Superemail paint.

Fig. 3B is a photograph of a rusty panel painted with two layers of the primer of the invention and Nirlat Supremail paint.

15 Fig. 4 is a photograph of a rusty panel, the upper portion of which is painted with the primer composition of the invention and Tambour® polyurethane-based paint; the lower portion is untreated.

Fig. 5 is a photograph of a rusty panel coated with three layers of the composition of the invention.

20 Fig. 6 is a photograph of a rusty panel, the lower portion of which is painted with two layers of the composition of the invention and with BASF's epoxy-based paint; the upper portion is untreated.

Fig. 7 is a photograph of a rusty panel painted with Tambour® antirust and Tambour® Eitan paint.

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## DETAILED DESCRIPTION OF THE INVENTION

In order to understand the invention and to see how it may be carried out in practice, some specific embodiments will now be described, by way of non-limiting examples only.

### EXAMPLE 1

A composition was prepared as follows: to 26 parts of phosphoric acid (40% in water) were added 2 parts of zinc molybdenum ortho phosphate hydrate and 1  
5 part of sodium chloride. The rest of the ingredients were added to the solution thus obtained.

0.4 parts of hydroxyethyl cellulose and 0.9 parts of WRACLA™ were mixed with 44 parts of water. To this solution were added 15 parts of zinc aluminum phosphate, 6 parts of barium sulphate and 6 parts of silicon oxide, and  
10 the mixture was thoroughly mixed to obtain a dispersion.

A ferrous oxide pigment was prepared by grinding 15 parts of micronized  $\text{Fe}_2\text{O}_3$  to 6-7 Hegman.

An alkyd resin was prepared from 50 parts vinyl acrylic copolymer (53-55% solids) and 50 parts of acrylic copolymer (46-50% solids) together with BYK 036,  
15 BYK 190 and BYK 380.

All the solutions were mixed together and the pH was stabilized at around 3.5.

#### EXAMPLES 2-4

The following table summarizes formulations of compositions prepared according to the invention:

Table 1

Parts	Example 1	Example 2	Example 3	Example 4
2	Zinc molybdenum orthophosphate hydrate	ZnO	Zn	Zn (2.1 parts)
1	NaCl	NaCl	NaCl	-
1	MgCl <sub>2</sub>	MgSO <sub>4</sub>	MgSO <sub>4</sub>	MgSO <sub>4</sub>
15	Zinc aluminum polyphosphate hydrate	Zinc molybdenum orthophosphate hydrate	Zinc molybdenum orthophosphate hydrate	Zinc molybdenum orthophosphate hydrate

All the other ingredients, quantities and methods of preparation are like those given under EXAMPLE 1 above. (Example 1 in the table is a repetition of EXAMPLE 1).

#### Testing examples 1-4

Coatings of the above-described compositions were applied to rusted metallic substrate panels by a brush. The coatings were applied in the amount 80-100 g/m<sup>2</sup> in a crosswise pattern. Two coats were applied with the drying time between each coat of 60 minutes. After that, the coatings were dried for 24 hours. After drying, the panels were placed into a salt spray cabinet with a concentration of 5% NaCl at a cabinet for 300, 500, 1000 and 1500 hours exposure and then tested. The properties tested included a flexibility test in accordance with ASTM D522, an adhesion test and general appearance test in accordance with Israeli Standard SI 785 Part 27. The panels coated by commercially available rust

### EXAMPLES 5-8

In table 4 below there are represented experimental results obtained with compositions of Example 2 above, where the stabilizer WRACLA was replaced by other stabilizers. The results are of tests performed as explained above.

Table 4

No.	Stabilizer	Quantity	100 hr. check out			300 hr. check out			500 hr. check out		
			1	2	3	1	2	3	1	2	3
5	BYK 154	0.1	Pass	0	Cracking no. 8	Pass	3	Cracking no. 4	-	-	-
6	Parmetol DF18	0.3	Pass	2	Blistering no. 6	Fail 20 mm	3	Rusting, blistering no. 8-1	-	-	-
7	Dispex A 40	0.4	Fail 23mm	3	Blistering no. 6	-	-	-	-	-	-
8	Propanol	0.3	Pass	2	No bubbles	Pass	2	Blistering no. 6	Pass	3	Bubbles No. 4

1. bend test (ASTM D 522-Flexibility)
2. adhesion (ASTM D 3359)
3. appearance (ASTM D 714-87,D 610)

### EXAMPLES 9 and 10

The thermal stability of the following compositions was checked and it was found that only at 250°C thermal deformations are induced in the composition of example 9, and in the composition of example 10, thermal deformations were induced only at 400°C. Both compositions had BYK 036 as a surfactant. The pH of the composition of example 9 stabilized on 3.1, and that of example 10 on 2.8. It may be generally stated that reducing the amount of alkyd resins in the

converting coatings were tested as well. The obtained results are summarized in tables 2 and 3 below.

Table 2

Coating	after 100 hrs in salt cabinet			after 300 hrs. in salt cabinet		
	Bend test	Adhesion	Appearance	Bend test	Adhesion	appearance
Example 1	Pass	0	Change color	Pass	2	No change
Example 2	Pass	0	Change color	Pass	4	Bubbles
Example 3	Pass	0	Change color	Pass	5	No change
Example 4	Pass	0	Change color	Pass	0	No change
Conventional						
Granville						Bubbles
Hammerite						Bubbles
T. Metal			Bubbles	Failed	5	Bubbles

Table 3

Coating	after 500 hrs in salt cabinet			after 1000 hrs. in salt cabinet			after 1500 hours in salt cabinet		
	Bend test	Adhes.	Appear.	Bend Test	Adh.	Appear.	Bend Test	Adh.	Appear.
Example 1	Pass	0	No change	Fail 15mm	2	no change	Fail 20mm	5	No change
Example 2	Pass	1	No change	Fail 25mm	4	no change	Fail 23 mm	5	No change
Example 3	Pass	1	Nochange	Fail 20 mm	2	no change	Good	5	No change
Example 4	Pass	0	No change	Fail 12mm	4	no change	Fail 17mm	1	No change
Conventional									
Granville			Bubbles			bubbles			bubbles
Hammerite			Cracks			bubbles			bubbles
T. Metal			Bubbles			bubbles			bubbles

composition allows for stability under higher temperatures, but may cause the coated layer to be more fragile. The formulations of the compositions of example 9 and 10 are given in table 5 below.

Table 5

Component	Parts in example 9	Parts in example 10
Phosphoric acid (40%)	26	24
MgSO <sub>4</sub>	1	1
Zinc powder	2	2.1
NaCl	1	
Hydroxyethylcellulose	0.4	0.4
Water	44	43
WRACLA <sup>®</sup> stabilizer	0.9	0.9
Zinc molybdenum orthophosphate hydrate	6	-
Zinc aluminum polyphosphate hydrate	-	8
BaSO <sub>4</sub>	6	6
SiO <sub>2</sub>	17	21
Fe <sub>2</sub> O <sub>3</sub>	15	15
Acrylic copolymer (46-50% solids)	46	40
Vinyl acrylic copolymer (53-55% solids)	46	40

## EXAMPLES FOR THE USE OF THE COMPOSITION AS A PRIMER

5 A primer composition was prepared according to the description in EXAMPLE 1 above and will be referred hereinafter as Killrust™.

Steel panels where Killrust™ was used as a primer were compared to similar panels where commercially available primers were used. The panels where Killrust™ was used as a primer had a rust layer of between 30 and 100 microns. 10 They were first cleaned by seawater and then dried and coated by Killrust™. The Killrust™ was applied on rusty panels, to obtain a coating thicker than the rust layer. The other panels were first pretreated to clean them from rust in accordance with the manufacturer's instructions, typically, by washing them with solvents such as distilled water, MEK (methyl ethyl ketone), acetone etc, and then dried and 15 coated with a commercially available primer, after they were clean of rust.

The primer composition of the present invention was tested in comparison with commercially known primers, such as Tambour Antirust, Zinchromate and Nirlat Zinchromate.

Paints that were applied over the said primer coatings were:

- 20 a. Epoxy: Ameron 400; Amercoat 300A; BASF 400; Tambour Epoxy; Nirlat Epoxy.
- b. Polyurethane: Ameron 450; BASF 600; Tambour polyurethane paint and Nirlat polyurethane paint.
- c. Alkyde-synthetic: Tambour Eitan; Nirlat Superemail 96.
- 25 d. Acrylic-PU: Rustoleum 5222; Nirlat Unicryl.

All tested paints applied over the primer of the invention (on rusted panels) showed results at least as good as when applied over a commercially recommended primer (on rust-clean panels). Therefore, the primer of the invention may be termed 30 a universal primer. Paints that adhere preferably to the primer according to the

invention are those that contain only small amounts of thinners such as nitrocellulose, more preferable are paints, which do not contain any such thinners.

Fig. 1A and its continuation, Fig. 1B, show a table of tests results of 11 panels, tested as per ASTM B-117, D610 and D-714. The tests were carried out on steel panels prepared as per manufacturers specifications. Where so indicated panels were rusted before application of the coatings. Killrust™ is the tradename used in the figures to indicate the composition of the invention. The data appearing in the table demonstrate, *inter alia*:

- ♦ the variety of paints that may be painted over the primer of the invention (see panels 5 to 10);
- ♦ the superiority of the composition of the invention in its applicability on rusted panels (panels 1 and 3 to 10);
- ♦ the efficiency of the composition of the invention as both primer and paint (panel 1); and
- ♦ the superiority of the composition of the invention over a commercially available combination of primer and paint (panels 10 and 11).

Figures 2 to 7 show photographs of some of the panels described in Figs. 1A and 1B, together with some additional panels as follows:

Figs. 2A, 2B and 2C show panels with Amerlock 400 epoxy paint, painted directly on rust (Fig. 2A, panel 3 in Fig. 1A), painted on rust-clean panel over a Tambour® antirust primer (Fig. 2B, not appearing in Fig. 1), and painted on a rusted panel over 2 layers of the primer of the invention (Fig. 2C, panel 6 in Fig. 1A). All photographs were taken after 1000 hours in a salt cabinet.

Figures 3A and 3B are photographs of panels 11 and 10, respectively, of Fig. 1B, at 1000 hours. It is clearly observed that the composition of the invention provides a better primer for the Nirlat Superemail paint than the Nirlat Zinchromate, recommended by the manufacturer, even though the composition of the invention was applied directly on a rusted surface.

Fig. 4 illustrates a steel panel treated with the composition of the invention as a primer and a polyurethane-based paint distributed by Tambour® (upper panel) and the same panel untreated (lower panel). The photograph illustrates that the primer of the invention may be safely used with polyurethane-based paints.

5        Figures 5 and 6 are panels photographed after 4000 hours in a salt cabinet. Figure 5 is a photo of a steel panel coated (when rusted) by three layers of the composition of the invention (panel 1 in Fig. 1A), and Figure 6 is a photo of a steel panel coated (when rusted) by two layers of the composition of the invention and one layer of a BASF's epoxy-based paint (panel 5 in Fig. 1A).

10        Figure 7 describes a panel with primer and paint not in accordance with the present invention (not mentioned in Figs. 1A and 1B), after 500 hours in a salt cabinet.

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